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# PATENT SPECIFICATION

1,100,261

NO DRAWINGS.

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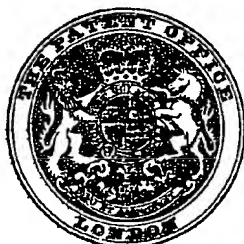
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## COMPLETE SPECIFICATION.

### Improvements in the Manufacture of Highly Fluorinated Aromatic Compounds.

I, MINISTER OF TECHNOLOGY, formerly Minister of Aviation, London, do hereby declare the invention, for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to the manufacture of highly fluorinated aromatic compounds, that is to say, aromatic compounds which have aromatic nuclei which are normally fully fluorinated but which may contain a low proportion of another halogen atom.

In accordance with the invention, a process for the manufacture of a highly fluorinated polyphenylene comprises reacting a Grignard reagent containing a fully fluorinated phenyl or polyphenyl group with a compound containing a fully fluorinated phenyl or polyphenyl group in the presence of tetrahydrofuran as solvent. The highly fluorinated polyphenylene is normally fully fluorinated but may contain a low proportion of the Grignard halogen atom.

The aromatic compound containing a fully fluorinated phenyl or polyphenyl group acts effectively as a polymer chain terminator when used at least in the order of ten molar per cent of the Grignard reagent. Perfluorobenzene, perfluorobiphenyl and perfluoroterphenyl can be used as chain terminators.

When the Grignard reagent is a perfluorinated phenylmagnesium halide the polyphenylene formed appears to contain a preponderance of highly-fluorinated *para*-phenylene linkages, but by using a Grignard reagent based on biphenyl, such as perfluorobiphenyl-3-magnesium bromide, a

polyphenylene may be formed containing a substantial proportion of highly fluorinated *meta*-phenylene linkages.

The required Grignard reagent,  $\text{RMgX}$ , is readily formed by reacting the appropriate halide,  $\text{RX}$  where  $\text{X}$  is either chlorine, bromine or iodine, with a large excess of magnesium in the cyclic ether tetrahydrofuran at temperatures usually employed for Grignard reagent formation.

The polymerisation does not proceed in the presence of a non-cyclic aliphatic ether either when tetrahydrofuran is or is not present. The fact that the presence of a cyclic ether is essential is confirmed by the fact that polymerisation proceeds not only in refluxing tetrahydrofuran, but also although more slowly at room temperature in tetrahydrofuran.

This reaction between a Grignard reagent containing a perfluorinated phenyl or polyphenyl group and an aromatic compound containing a perfluorinated phenyl or polyphenyl group in the presence of tetrahydrofuran can be used to produce highly fluorinated polyphenylenes of various degrees of polymerisation from three up to 25 or more by controlling the relative proportions of the Grignard reagent and the aromatic compound. When there is a relatively high proportion of Grignard reagent, e.g. a molar excess up to about ten to one, the product normally comprises mainly highly fluorinated polyphenylenes of relatively high molecular weight (degree of polymerisation of about 25) and when there is a relatively high proportion of aromatic compound the product normally comprises mainly highly fluorinated polyphenylenes which are lower polyphenyls, for example, highly fluorinated

terphenyls and quaterphenyls. By suitable selection of the proportions of the two reactants and also suitable selection of the aromatic compound a desired polyphenylene may be made to predominate in the product.

For example, with 10 moles per cent of aromatic compound the principal product is a polyphenylene having a degree of polymerisation of about 25, together with some octiphenyl and septiphenyl. On the other hand if the aromatic compound is a biphenyl and the Grignard reagent is a phenyl magnesium halide and there are two moles of aromatic compound to one mole of Grignard reagent the main product is terphenyl with some quaterphenyl and a little quinquephenyl.

When pentafluorophenyl magnesium bromide is reacted with decafluorophenyl in accordance with the invention the main product is perfluoro-p-terphenyl together with some perfluoro-p-quaterphenyl and a little perfluoro-p-quinquephenyl.

In order to illustrate the invention, various reactions between pentafluorophenyl magnesium bromide and hexafluorobenzene, decafluorobiphenyl or perfluoro-p-terphenyl will now be described by way of example only.

	(i) at 70—80°C/20mm	m.p. 67—68°C	—	16.95 g
60	(ii) at 115—130°C/0.05mm	m.p. 191—193.5°C	—	4.08 g
	(iii) at 160°C/0.05mm	m.p. 231—232°C	—	0.82 g
	(iv) at 200°C/0.05mm	m.p. 291—303°C	—	0.34 g

Fraction (i) was unreacted decafluorobiphenyl.

Fraction (ii) was perfluoro-p-terphenyl which after purification had m.p. 193—194°C (Found C, 44.5; F, 55.1;  $C_{18}F_{14}$  requires C, 44.8; F, 55.2%). The yield was 2.55g (7.4%).

Fraction (iii) was perfluoro-p-quaterphenyl which after purification had m.p. 233—234.5°C (found C, 45.4; F, 54.1;  $C_{24}F_{18}$  requires C, 45.7; F, 54.3%).

Fraction (iv) was perfluoro-p-quinque-

	(i) Up to 250°C	2.4%, m.p.	307°—309°C
	(ii) 250°—300°C	51.9%, m.p.	at least 340°C
	(iii) 300°—350°C	4.2%, m.p.	at least 411°C
90	(iv) Over 350°C	38.0%, m.p.	at least 423°C

Fractions (ii), (iii) and (iv) were bromine-free and gave analyses corresponding to  $C_nF_n(C_6F_5)_n$  wherein "n" is respectively 5, 6 and 23.

It will be noted that the polyphenylenes are produced without refluxing the reaction mixture. If the reaction mixture is refluxed (e.g. for eight hours) in the tetrahydrofuran a very similar range of products is obtained.

Pentafluorophenyl magnesium bromide required for the reactions was prepared as follows, under an atmosphere of dry nitrogen. Magnesium turnings (10.75g) in dry tetrahydrofuran (37.5 ml) were cooled to -12°C and bromopentafluorobenzene (8.65g, 0.035 M) in tetrahydrofuran (56 ml) was added rapidly with stirring. A strong exothermic reaction began almost immediately and was controlled (max. internal temp. 1.5°C) by use of a cooling bath at -70°C. After the reaction had died down (about 5 min) stirring was continued at 0°C for ½ hour and after cooling to -10°C the solution was filtered directly into an addition funnel.

#### Example 1

Decafluorobiphenyl (23.4g, 0.07 M) in dry tetrahydrofuran (110 ml) under an atmosphere of dry nitrogen was stirred while the cooled Grignard solution (prepared as described above and diluted to 115 ml) was added during 40 min; the temperature did not exceed 21°C. After 26 hours without stirring the solution was poured into water (2 l), the white precipitate collected, washed with water, dried and sublimed *in vacuo* to yield the following fractions:—

phenyl, which after purification had m.p. 299—304°C.

#### Example 2.

Perfluorophenylmagnesium bromide (0.31 M, prepared at 0°C) was reacted with decafluorobiphenyl (0.031 M) at room temperature for about 40 hours and a polymeric product was produced of which 92% was insoluble in tetrahydrofuran. This insoluble product was substantially free of bromine and gave the following fractions on sublimation *in vacuo*.

#### Example 3.

A polymeric product was prepared by reacting perfluorophenylmagnesium bromide (0.31 M, prepared at 0°C) with perfluorobenzene (0.031 M) in refluxing tetrahydrofuran for eight hours, and gave the following fractions by wt. on sublimation *in vacuo* of the material insoluble in tetrahydrofuran (86%):—

- (i) Up to 300°C 11%  
 (ii) 300°—400°C 26%  
 (iii) Over 400°C 63%

*Example 4.*

- 5 Perfluoro-p-terphenyl (2.00g, 0.004 M)  
 was dissolved in dry tetrahydrofuran (50

ml). Pentafluorophenyl-magnesium bromide (0.002 M in tetrahydrofuran 5.4 ml) was then added and the mixture kept at room temperature for 65 hours. The mixture was poured into water (500 ml), the white precipitate collected, dried and sublimed *in vacuo* to yield the following fractions:—

- |    |                         |                   |         |
|----|-------------------------|-------------------|---------|
| 15 | (i) at 100—120°/0.05mm  | m.p. 192—194°     | 1.38 g  |
|    | (ii) at 128—138°/0.05mm | m.p. 233.5—234.5° | 0.25 g  |
|    | (iii) at 145°/0.05mm    | m.p. 227—339.5°   | 0.028 g |
|    | (iv) at 160—175°/0.05mm | m.p. 292°—301°    | 0.01 g  |

Fraction (i) was unreacted perfluoroterphenyl.

- 20 Fraction (ii) was perfluoro-p-quaterphenyl identical with authentic material.

Fraction (iv) was impure perfluoro-p-quinquephenyl.

- 25 The various polyphenylenes produced from a perfluorinated Grignard reagent prepared under conventional conditions as above described although well-defined products with low Grignard halogen content, are all relatively insoluble in solvents including tetrahydrofuran and do not have a high degree of polymerisation.

- 30 The conditions under which the perfluorinated Grignard reagent is prepared has a pronounced effect on the properties of any polymeric product and conditions have been found by which polymeric products can be obtained from perfluorinated Grignard reagents which are highly soluble in tetrahydrofuran. As a result these highly fluorinated polyphenylenes can be cross-linked with difunctional nucleophilic reagents (e.g. alkali salts of diphenols or diamines) in a solution reaction.

- 45 In accordance with a feature of the invention, a process for the manufacture of a highly fluorinated polyphenylene which is soluble in tetrahydrofuran comprises reacting at a temperature below -20°C a highly perfluorinated phenyl or polyphenyl halide (where the halide is chloride, bromide or iodide) with magnesium in a molar excess of at least 50 per cent in the presence of at least one litre of tetrahydrofuran for each molar proportion in grams of the phenyl or polyphenyl halide, refluxing the resulting solution for at least one hour, and extracting the highly fluorinated polyphenylene from the tetrahydrofuran.

- 60 The reaction is carried out preferably at a temperature of about -30°C and to obtain an increased yield of higher molecular weight polymeric material the solution should be refluxed for at least six hours.

- 65 By way of example, the preparation of a polymer soluble in tetrahydrofuran will now be described.

*Example 5.*

Bromopentafluorobenzene (9.27 g, 0.0375 M), magnesium turnings (95 g) and tetrahydrofuran (200 ml), under dry nitrogen, were cooled to -54°C. (The magnesium turnings if desired may have been preactivated by reaction with bromobenzene in tetrahydrofuran followed by thorough washing with the solvent.) A further quantity of bromopentafluorobenzene (64.86 g, 0.2635 M) in tetrahydrofuran (600 ml) was added dropwise over 30 mins. with stirring. The exothermic reaction was controlled by a -70°C bath and the rate of addition so that the temperature was maintained at -30°C (the maximum internal temperature was -24°C). Stirring was continued for 1½ hours while the temperature was maintained at -30°C after which the mixture was allowed to stand for one hour and was then filtered through glass paper pulp under nitrogen. The filtrate (550 ml) was refluxed for 8 hours under nitrogen and then hydrolysed with 400 ml. of 2N hydrochloric acid. The mixture was added to water and filtered and the resulting precipitate washed to yield 25.65 g of an ochre powder which was 95 per cent soluble in tetrahydrofuran.

## WHAT I CLAIM IS:—

1. A process for the manufacture of a highly fluorinated polyphenylene which comprises reacting a Grignard reagent containing a perfluorinated phenyl or polyphenyl group with a compound containing a perfluorinated phenyl or polyphenyl group in the presence of tetrahydrofuran as solvent.

2. A process according to Claim 1 wherein the said compound is hexafluorobenzene, perfluorobiphenyl or perfluoroterphenyl.

3. A process for the manufacture of a highly fluorinated polyphenylene which is soluble in tetrahydrofuran and which comprises reacting at a temperature below -20°C a perfluorinated phenyl or polyphenyl halide with magnesium in a molar excess of at least 50 per cent in the pre-

sence of at least one litre of tetrahydrofuran for each molar proportion in grams of the phenyl or polyphenyl compound, refluxing the resulting solution for at least one hour, and extracting the highly fluorinated polyphenylene from the tetrahydrofuran.

4. A process according to Claim 4 wherein the reaction between a perfluorinated phenyl or polyphenyl halide and magnesium is carried out at about  $-30^{\circ}\text{C}$ .

5. A process according to either Claim 4 or 5 wherein the said resulting solution is refluxed for at least six hours.

6. A process for the manufacture of a

highly fluorinated polyphenylene substantially as hereinbefore described in any one of the examples.

7. A highly fluorinated polyphenylene when made by a process in accordance with any preceding claim.

8. A fully fluorinated polyphenylene when made by a process in accordance with any one of Claims 1 to 8.

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